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Thermal Stability of the Carbon-Carbon Bond in Ethylene
Adsorbed on Si(100): An Isotopic Mixing Study

by

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Abstract

The dominant surface chemical process involving chemisorbed C₂H₄ on Si(100) is the desorption of the intact C₂H₄ molecule. By studying the isotopic mixing between ¹³C₂H₄ and ¹²C₂H₄ to produce ¹³CH₂-¹²CH₂, it has been shown that less than 1% isotopic mixing occurs in the temperature range 500-950 K. This observation excludes the recombination process 2CH₂(a) + C₂H₄(a) → C₂H₄(g) as being of importance in C₂H₄ desorption from Si(100).

In addition, the efficiency, η^{SiC} , of SiC formation from C₂H₄ has been carefully remeasured using direct calibration of the Auger spectrometer for adsorbed carbon using C₂H₄ of known absolute coverage as a standard. We find that $\eta^{\text{SiC}} = 3.3 \times 10^{-3}$ SiC units per C₂H₄ collision at a Si(100) temperature of 950 K.

I. INTRODUCTION

The interaction of ethylene with the Si(100) surface has been studied in ultrahigh vacuum using a variety of surface science techniques [1-5] to investigate the surface complex produced and the nature of the high temperature SiC thin film growth process on the Si(100) surface. Recent studies have shown that on a perfect Si(100) surface a single C_2H_4 molecule adsorbs on a Si dimer (Si_2) site at saturation coverage [5], and a di- σ -surface bonding model has been proposed based on the absence of the C=C bond in this adsorbed species as determined by HREELS [2].

Studies of the chemical vapor deposition of SiC thin films on Si(100) have shown that the efficiency of SiC formation, η^{SiC} , is very low in the temperature range 890-1140 K. Thus, Bozso et al [1] measured at 940 K, where the optimum SiC film growth rate was found, that the efficiency of SiC formation per C_2H_4 collision with Si(100) was $\eta^{SiC} = 2 \times 10^{-3}$. More recently, Taylor et al [4] measured an initial efficiency of $\eta^{SiC} = 2 \times 10^{-5}$ SiC units per C_2H_4 collision at 970 K. Both of these measurements indicate that near 1000 K the vast majority of C_2H_4 molecules incident on Si(100) are unreactive, as judged by the low rate of formation of SiC.

The investigation reported here was performed in the temperature range 550-950 K to determine whether in ethylene-derived surface species, carbon-carbon bond scission occurs on Si(100), followed by recombination of $CH_2(a)$ fragments. One might postulate that the low efficiency of C_2H_4 conversion to SiC is due to an efficient recombination reaction $2CH_2(a) + C_2H_4(a) \rightarrow C_2H_4(g)$, much like the well-known adsorbate atom recombination reactions on metal surfaces at high tem-

peratures [$2\text{N}_2(\text{a}) \rightarrow \text{N}_2(\text{g})$; $2\text{O}_2(\text{a}) \rightarrow \text{O}_2(\text{g})$ etc.] [6,7].

In this investigation we have performed two types of experiments. In the first experiment, equimolar quantities of $^{13}\text{C}_2\text{H}_4$ and $^{12}\text{C}_2\text{H}_4$ were coadsorbed on the Si(100) surface at 105 K. Temperature programmed desorption (TPD) of $\text{C}_2\text{H}_4(\text{g})$ was carried out, searching for any isotopic mixing to produce $^{13}\text{CH}_2=^{12}\text{CH}_2(\text{g})$ (at 500-650 K). In the second experiment, which investigated the possibility of isotopic mixing at a higher temperature, a beam containing equal quantities of the two isotopic ethylene species was directed at the Si(100) crystal at 950 K, and the reflected (and desorbing) C_2H_4 was studied to detect any isotopic mixing. Both experiments yielded negative results. The absence of $^{13}\text{CH}_2=^{12}\text{CH}_2$ formation therefore indicates that a $\text{CH}_2(\text{a})$ recombination process does not occur in the temperature range 500-950 K, and that the major kinetic process liberating C_2H_4 from Si(100) involves only $\text{C}_2\text{H}_4(\text{a}) \rightarrow \text{C}_2\text{H}_4(\text{g})$.

II. EXPERIMENTAL

The ultrahigh vacuum (UHV) apparatus used in this study (base pressure 4×10^{-11} torr) has been described previously [5]. The system is equipped with a Perkin Elmer single-pass cylindrical mirror analyzer (CMA) Auger spectrometer, an argon ion sputtering gun, a collimated and accurately calibrated microcapillary array beam doser[5,8], and a UTI-100C quadrupole mass spectrometer (QMS) which is shielded from direct line-of-sight to the crystal in order to study the random flux of gas originating from the crystal [9]. The apparatus is also equipped with a movable shutter which can be quickly positioned in or out of the C_2H_4 beam in order to control exposure of the crystal to the beam. The

mounting of the Si(100) crystal (14.95 x 14.95 x 1.5 mm; p type; B doped; 10 Ω -cm), as reported elsewhere [5,8], provides excellent thermal contact between the crystal and the liquid nitrogen-cooled Cu mounting block, permitting a crystal temperature of 105 K to be reached. In situ cleaning by argon ion bombardment followed by heating to 1190 K, as described previously [5], has been shown to result in a reproducible Si(100) surface containing a defect density of ~25%, as judged by its quantitatively constant capacity to chemisorb ethylene and acetylene at 105 K.

The research grade ethylene (99.99% pure, 97.8% isotopic $^{12}\text{C}_2\text{H}_4$, from Matheson) and ethylene-1,2- ^{13}C (92.1 atom% ^{13}C , from MSD Isotopes) were further purified by several freeze-pump-thaw cycles. The gas molecules were delivered, with a known absolute incident flux, to the crystal surface through the beam doser [5,8]. Knowing the absolute effusion rate through the doser and the geometric relation between the crystal and the doser [10,11] allows a direct determination of the absolute number of molecules adsorbed on the surface as a function of exposure [5].

Three types of experiments involved the use of the mass spectrometer for measurements. These are: (1) ethylene adsorption at 105 K; (2) temperature programmed desorption in the temperature range 500-650 K; and (3) a high temperature study at 950 K when an ethylene beam is incident on the Si(100) surface. Data were acquired with the multiplexed QMS driven by a Teknivent mass spectra data system. This PC-DOS based system allows for real-time, interactive data acquisition with simultaneous detection of several masses. In this study, data acquisition usually occurred at a sampling rate of 1-8 masses/second. A

linear temperature ramp between 105-1000 K, for temperature programmed desorption measurements, is provided by a Honeywell UDC-500 temperature controller used to drive a feedback circuit to control the power to the crystal [12]. During the high temperature study in which the crystal was exposed to the ethylene beam, the crystal was heated with the same power supply which was able to maintain the crystal temperature at 950 ± 5 K.

III. RESULTS AND DISCUSSION

A. Coadsorption of Reactants and Coverage Measurement

For the series of simultaneous coadsorption experiments which follow, a mixed reactant source containing 50%-50% " $^{13}\text{C}_2\text{H}_4$ " and " $^{12}\text{C}_2\text{H}_4$ " was used. The gas mixture was prepared in the gas storage line behind the doser assembly by adding an equal number of moles of " $^{13}\text{C}_2\text{H}_4$ " and " $^{12}\text{C}_2\text{H}_4$ " to the storage volume.

The partial pressure change during adsorption of the mixed reactant on the Si(100) surface at 105 K was detected using the QMS to monitor the random flux of ethylene (and some of its cracking products). The masses monitored are $m/e = 25-30$ which are the major cracking patterns of the isotopic gases and can represent the isotopic abundance of the isotopic ethylene gases, $^{13}\text{C}_2\text{H}_4$, $^{13}\text{CH}_2=\text{}^{12}\text{CH}_2$, and $^{12}\text{C}_2\text{H}_4$, present in the UHV chamber [13].

Details about the adsorption kinetics and the absolute coverage measurement of ethylene on Si(100), using the beam dosing technique with random flux detection, have been described elsewhere [5]. Briefly, the adsorption of the ethylene mixture onto Si(100) at 105 K is indicated by the drop of QMS signal upon removing the shutter between the beam of the ethylene mixture and the Si(100) crystal (open shutter), as shown in

Figure 1. The rapid initial drop is followed by a constant QMS signal indicating a constant probability of adsorption (reaction probability = 1) for the initial adsorption of ethylene on Si(100) at 105 K in the uptake region [5]. The surface coverage achieved can be controlled by closing the shutter at an appropriate exposure. The absolute coverage, $N(t)$, deposited on the crystal can then be determined [5] from the analysis of the uptake curve according to Equation (1).

$$N(t) = (F+F_r) \int S(t) dt \quad (1)$$

Here F is the beam flux onto the crystal (molecules/cm²s), F_r is the background random flux ($F_r = 0.009 F$), and $S(t)$ is the reaction probability. In the particular experiment shown in Figure 1, the shutter is closed when the total C_2H_4 coverage is 0.24 C_2H_4/Si_2 on the Si(100) surface.

For clarity, in the adsorption experiment shown in Figure 1, only masses of 30, 29, and 28 are shown, which represent the parent mass spectral cracking products of $^{13}C_2H_4$, $^{13}CH_2-^{12}CH_2$, and $^{12}C_2H_4$ respectively [13]. However, an additional issue must be addressed in determining the isotopic abundance from the cracking patterns of the gas molecules. Mass 30 represents only $^{13}C_2H_4^+$ (from $^{13}C_2H_4$) in this study. However, mass 29 is a combination of $^{13}C_2H_3^+$ (from $^{13}C_2H_4$) and $^{13}CH_2^{12}CH_2^+$ (from $^{13}CH_2^{12}CH_2$, if any), and mass 28 is a combination of $^{12}C_2H_4^+$ (from $^{12}C_2H_4$), $^{13}C^{12}CH_3^+$ (from $^{13}CH_2^{12}CH_2$, if any), and $^{13}C_2H_2^+$ (from $^{13}C_2H_4$). There is also a small background contribution from CO present in the UHV system in the low 10^{-11} torr range. Even with such complexity, any change of the isotopic abundance in desorption products due to production and desorption of $^{13}CH_2-^{12}CH_2$ will result in a signi-

ficant change of the mass spectrometric ratios compared to those measured during adsorption of the isotopic ethylene mixture at 105 K, as will be discussed below. The ratios of mass spectral cracking products are determined during adsorption from the relative areas of the uptake region for each mass.

B. Temperature Programmed Desorption Products from $C_2H_4/Si(100)$

Figure 2 shows the typical thermal desorption spectra from ethylene adsorbed on the Si(100) surface at 105 K. The only desorption species detected are ethylene and a small quantity of molecular hydrogen by temperature programmed heating to 900 K. The very small relative yield of H_2 compared to C_2H_4 indicates that the major reaction channel involving ethylene adsorption on Si(100) at 105 K is the desorption of molecular ethylene, since the ethylene decomposition channel will yield surface hydrogen which desorbs above ~ 700 K.

The thermal desorption method was used to study the isotopic mixing in the ethylene product after the simultaneous coadsorption of " $^{13}C_2H_4$ " and " $^{12}C_2H_4$ " on the Si(100) surface at 105 K. Figure 3 shows the TPD spectra of the isotopic ethylene desorption products resulting from the coadsorption of the mixed ethylene reactants which has been shown in Figure 1. Again, only masses of 30, 29, and 28 are shown in Figure 3. The same experiments, coadsorption followed by thermal desorption, were performed at four different submonolayer surface coverages. The measured mass spectrometric ratios (from mass 25 to mass 30) of the adsorbed reactants and the corresponding desorption products in the four individual experiments are listed in Table 1. The data for each mass was obtained from the integrated area of the uptake region for each mass

as monitored from the adsorption measurements (for reactants), or from the integrated areas of the desorption peaks (for products). In each case, the reactant and product yields for mass 25, 26, 27, 29, and 30 are normalized to the corresponding area of mass 28, with a small correction being made to the 28 amu uptake experiment due to the presence of background CO. Comparisons of all of the measured mass spectrometric ratios of reactants and desorption products clearly indicate that to within experimental error ($\pm 2\%$ isotopic mixing based on mass 29 yield) no isotopic mixing between ethylene-derived surface species occurs during temperature programmed desorption.

To be able to analyze the sensitivity of the isotopic mixing experiments where several isotopic ethylene species are monitored, a calculation was done by assuming various percentages of isotopic mixing (completely random mixing) in the desorbing ethylene. The results of the experiments and the calculation are summarized in Figure 4 which shows the mass spectrometric ratios of each desorption product based on the average of the four individual experiments as listed in Table 1 (the filled symbols) as well as the expected ratios based on the quantitative adsorption measurements and a calculation for various percentages of isotopic mixing in the desorbing products (the open symbols). For clearness, the results of mass 25, which have a similar trend to mass 30, are not shown in Figure 4. In the calculation, the mass spectroscopic ratios for 0% isotopic mixing was obtained from the measured cracking patterns of reactants (the average of the four adsorption experiments). If there is any isotopic mixing due to the reaction, not only the measured mass spectroscopic ratios of the reactants and the products will differ from each other, but also a significant positive or

negative trend for each mass will be expected as the percentage of the isotopic mixing increases. These results show that the highest sensitivity ($\pm 2\%$) may be obtained by monitoring mass 29, and that the behavior of mass 29 observed is opposite to that expected for isotopic mixing.

C. High Temperature C₂H₄ Isotopic Mixing Experiment

Based on the thermal desorption studies, it is apparent that the molecular desorption of ethylene from Si(100) does not occur via a CH₂(a) recombination process in the temperature range 500-650 K. To investigate the possibility that at higher temperatures the ethylene gas molecules striking a hot Si(100) surface can dissociate to produce CH₂(a) fragments which could be mobile and then recombine (CH₂(a)+CH₂(a)) to leave the surface as C₂H₄(g), the isotopic mixing method was therefore used at a steady substrate temperature of 950 K where the optimum SiC film growth rate was found [1].

During the experiment, the crystal temperature was kept constant at 950 K and the filament of the QMS was the only thermionic emitter operating in the UHV chamber. The isotopic gas mixture was initially admitted via the doser to the chamber with the crystal (at 950 K) shielded by the shutter. The average incident flux of ethylene on the Si(100) crystal during the experiment is 7.2×10^{12} C₂H₄/cm²s, calculated from the measured C₂H₄ flow rate into the doser and the known geometric relation between the crystal and the doser [5,10,11]. After a stable ethylene pressure was established (300 seconds), the shutter was moved out of the gas beam, and the crystal at 950 K was then exposed to the direct flux without any interruption for 60 minutes until an exposure of

$2.6 \times 10^{16} \text{ C}_2\text{H}_4/\text{cm}^2$ had been received by the crystal. At this point the shutter was closed. Figure 5 shows the mass spectrometric ratios during the high temperature process at 950 K as a function of exposure to the ethylene mixture. The data, during the time the crystal was shielded, represent the mass spectrometric ratios of reactants and are shown for every 30 seconds. The data, during the time the crystal was exposed to the isotopic ethylene gas beam, represent the mass spectrometric ratio of products and are shown as average values every 120 seconds for the purpose of clarity. A long term downward drift of less than 3% in the worst case (mass 27) clearly indicates that no recombination process occurs during the high temperature study at 950 K. This conclusion is substantiated by even smaller changes immediately upon opening and closing the shutter at the beginning and the end of the exposure to isotopic ethylene, where long term drifts are not involved.

An analysis of the sensitivity of the isotopic mixing experiments for the high temperature study was done in a similar manner to the thermal desorption study. The analysis is summarized in Figure 6. Based on the comparison of the results for reactants and products, our studies show no detectable production of $^{13}\text{CH}_2 = ^{12}\text{CH}_2$ (less than 1% isotopic mixing could be present based on the mass 29 behavior).

D. Efficiency of SiC Formation from C_2H_4 on Si(100) at 950 K

The efficiency of SiC formation from ethylene interaction with Si(100) at 950 K is estimated using Auger spectroscopy. The estimate is based on the intensities of the C(KLL) and the Si(LVV) Auger signals. Figure 7(a) shows the Auger spectrum of a clean Si(100) surface, whereas

Figures 7(b) and 7(c) show the C(KLL) signal after the crystal was exposed to $(2.6 \pm 0.2) \times 10^{16} \text{ C}_2\text{H}_4/\text{cm}^2$ at 950 K.

From previous Auger measurements of the adsorption of C_2H_4 on Si(100) [5] we can accurately calibrate the Auger intensity in absorbate fashion. A monolayer of C_2H_4 , corresponding to $5.0 \times 10^{14} \text{ C atoms/cm}^2$ on this Si(100) crystal (25% defects), yields a C(KLL)/Si(LVV) Auger intensity ratio of 0.037 ± 0.001 . Thus, assuming that all of the deposited carbon is present on the surface of the Si(100) crystal, we estimate from the Auger ratio shown in Figure 7(c) that the carbon coverage is $(8.5 \pm 1.1) \times 10^{13} \text{ C atoms/cm}^2$. The average efficiency of carbon deposition at 950 K is then

$$\begin{aligned} \eta_{\text{SiC}} &= \frac{(8.5 \pm 1.1) \times 10^{13} \text{ C atoms/cm}^2}{(2.6 \pm 0.2) \times 10^{16} \text{ C}_2\text{H}_4/\text{cm}^2} & (2) \\ &= (3.3 \pm 0.5) \times 10^{-3} \text{ C atoms/C}_2\text{H}_4 \text{ collision} \\ &= (3.3 \pm 0.5) \times 10^{-3} \text{ SiC units/C}_2\text{H}_4 \text{ collision.} \end{aligned}$$

Since at 950 K some carbon penetration into Si(100) may occur, this efficiency is a lower limit. We know from previous work [4] that the growth rate of SiC layer at 970 K (as judged by the C(1s) XPS intensity) is initially linear in this coverage region of SiC formation; the SiC formation efficiency measurement shown here is in the early part of the linear growth region, justifying the method of calculation in Equation (2).

IV. CONCLUSIONS

The adsorption of and isotopic mixing between $^{13}\text{C}_2\text{H}_4$ and $^{12}\text{C}_2\text{H}_4$ has been studied on Si(100). Using careful mass spectrometric studies of the production of $^{13}\text{CH}_2 - ^{12}\text{CH}_2$, it was determined that isotopic mixing is

absent (to an accuracy of 1-2%) in the temperature range 500-950 K.

Thus, the dominant surface process, C_2H_4 desorption, occurs by a mechanism which does not involve the random recombination of $CH_2(a)$ species.

In addition, the efficiency of SiC formation at the optimum decomposition temperature (950 K) has been measured to be $\eta^{SiC} = 3.3 \times 10^{-3}$ SiC units per C_2H_4 collision with the $Si(100)$ surface, which may be compared with previous measurements (ref. 1, $\eta = 2 \times 10^{-3}$ at 940 K; ref. 3, $\eta = 7 \times 10^{-4}$ at 1062 K and 1227 K; ref. 4, $\eta = 2 \times 10^{-5}$ at 970 K). This Auger measurement has been carefully calibrated against quantitative C_2H_4 adsorption measurements [5], and a more exact definition of the beam flux is present in this work compared to the earlier studies [1,4].

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Figure Captions

Figure 1. Simultaneous coadsorption of the mixed reactant of 50%-50% $^{13}\text{C}_2\text{H}_4$ and $^{12}\text{C}_2\text{H}_4$ on Si(100) at 105 K. The surface coverage is proportional to the uptake area. See Table 1 for the measured mass spectrometric ratio of each mass compared to 28 amu.

Figure 2. Typical thermal desorption spectra of C_2H_4 and H_2 from C_2H_4 adsorbed on Si(100) at 105 K. The QMS signals shown are not corrected for mass spectrometer sensitivity.

Figure 3. Temperature programmed desorption spectra after the simultaneous coadsorption of the ethylene mixture on Si(100) at 105 K. The integrated area of each mass was used to calculate the mass spectrometric ratio compared to 28 amu (see Table 1).

Figure 4. The sensitivity of the isotopic mixing method in the thermal desorption experiments. The filled symbols were measured from the desorption products. The open symbols were based on the calculations by assuming various percentage yields of the isotopic exchange products, where the 0% isotopic exchange was measured from the adsorption of reactants.

Figure 5. The measured mass spectrometric ratios for the isotopic ethylene mixture during reaction on Si(100) at 950 K as a function of exposure time. The average incident flux of ethylene is $7.2 \times 10^{12} \text{ C}_2\text{H}_4/\text{cm}^2\text{s}$.

Figure 6. The sensitivity of the isotopic mixing experiments for isotopic ethylene exposure to Si(100) at 950 K. The filled symbols were measured during exposed to ethylene. The open symbols

were based on calculations by assuming various percentage yields of the isotopic mixing products, where the 0% isotopic exchange was obtained from a study of reactants (crystal shielded regions in Figure 5).

Figure 7. Auger C(KLL) spectra of (a) the clean Si(100) surface at 105 K; (b) and (c) the Si(100) surface after exposure to 2.6×10^{16} C₂H₄/cm² at 950 K. The Si(LVV) signal is shown as a reference with an amplification factor of 1.

Table 1. Measured Mass Spectrometric Ratios of Adsorption Reactants and Desorption Products

Coverage (C ₂ H ₄ /Si ₂)		30	29	28	Mass		25
					27	26	
0.13	Adsorption	0.46	0.40	1.00	0.53	0.46	0.11
	Desorption	0.45	0.39	1.00	0.53	0.44	0.12
0.24	Adsorption	0.48	0.41	1.00	0.55	0.46	0.12
	Desorption	0.48	0.40	1.00	0.53	0.45	0.12
0.39	Adsorption	0.49	0.42	1.00	0.55	0.46	0.12
	Desorption	0.48	0.41	1.00	0.55	0.46	0.12
0.53	Adsorption	0.51	0.43	1.00	0.54	0.46	0.11
	Desorption	0.52	0.42	1.00	0.54	0.44	0.11

SIMULTANEOUS ADSORPTION OF THE 50%-50% MIXTURE OF
 $^{13}\text{C}_2\text{H}_4$ (30 AMU) AND $^{12}\text{C}_2\text{H}_4$ (28 AMU) ON Si(100) AT 105K

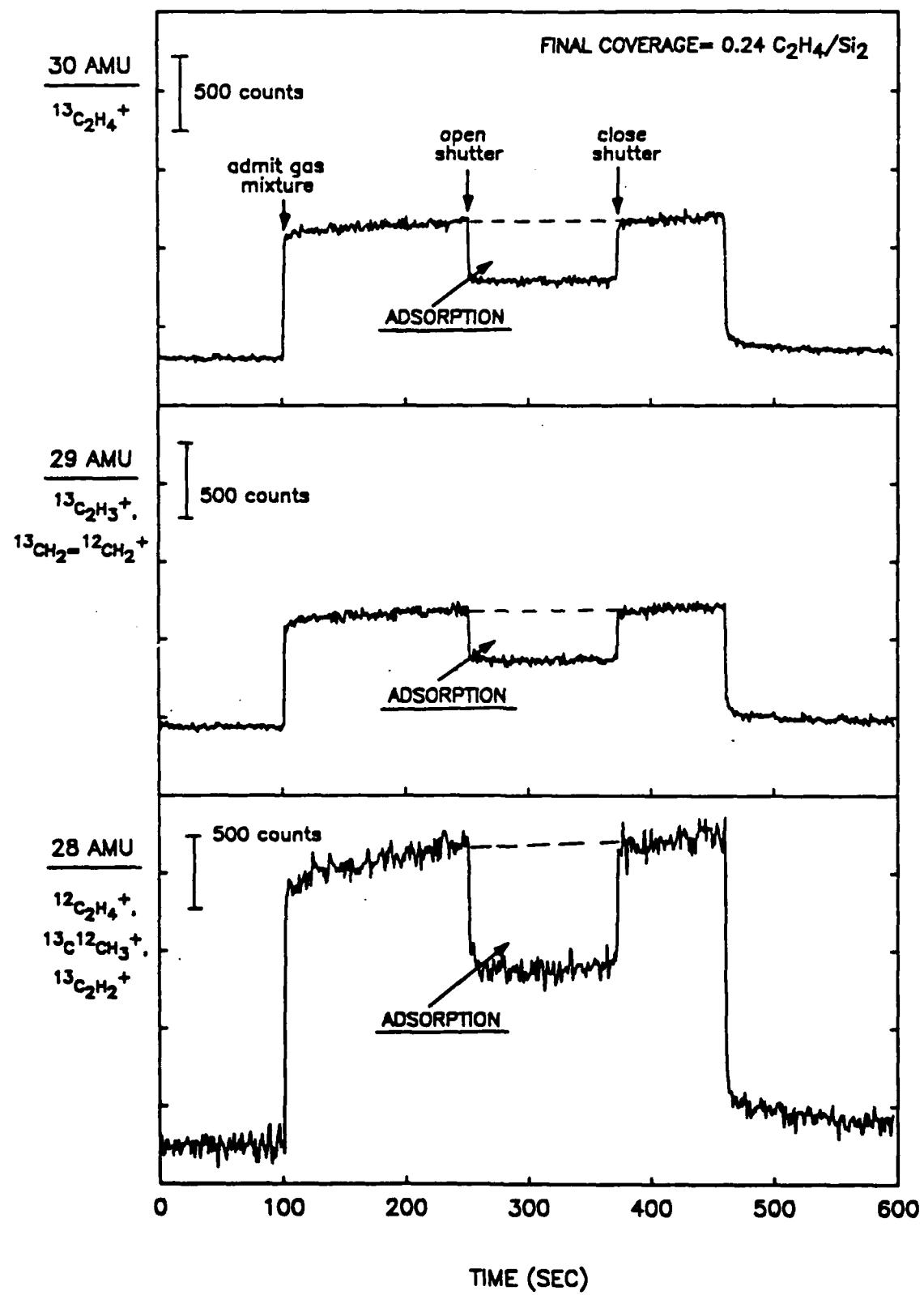
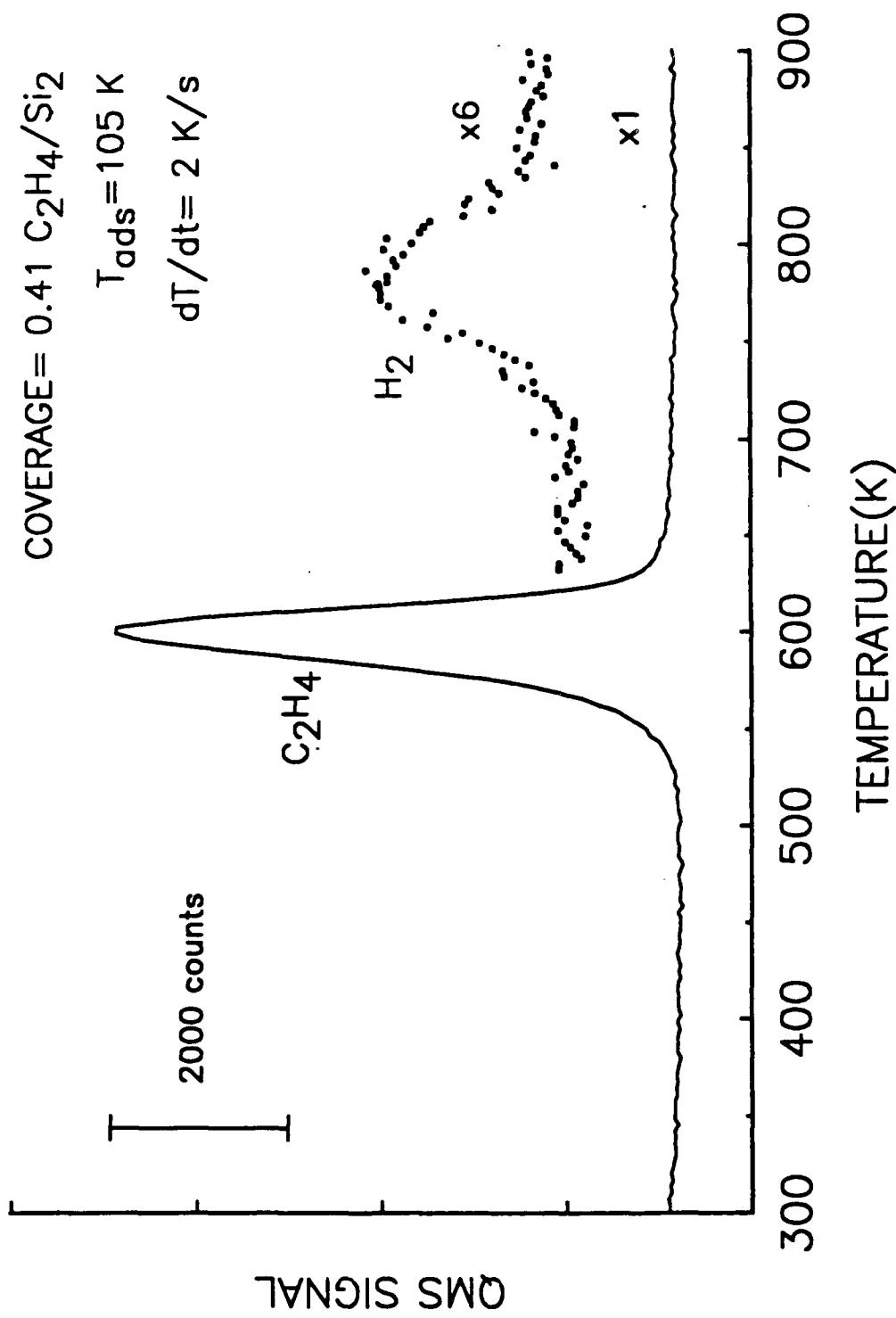


Figure 1
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TEMPERATURE PROGRAMMED DESORPTION --- C₂H₄/Si(100)



TEMPERATURE PROGRAMMED DESORPTION AFTER
SIMULTANEOUS COADSORPTION OF THE ISOTOPIC ETHYLENE
MIXTURE ON Si(100)

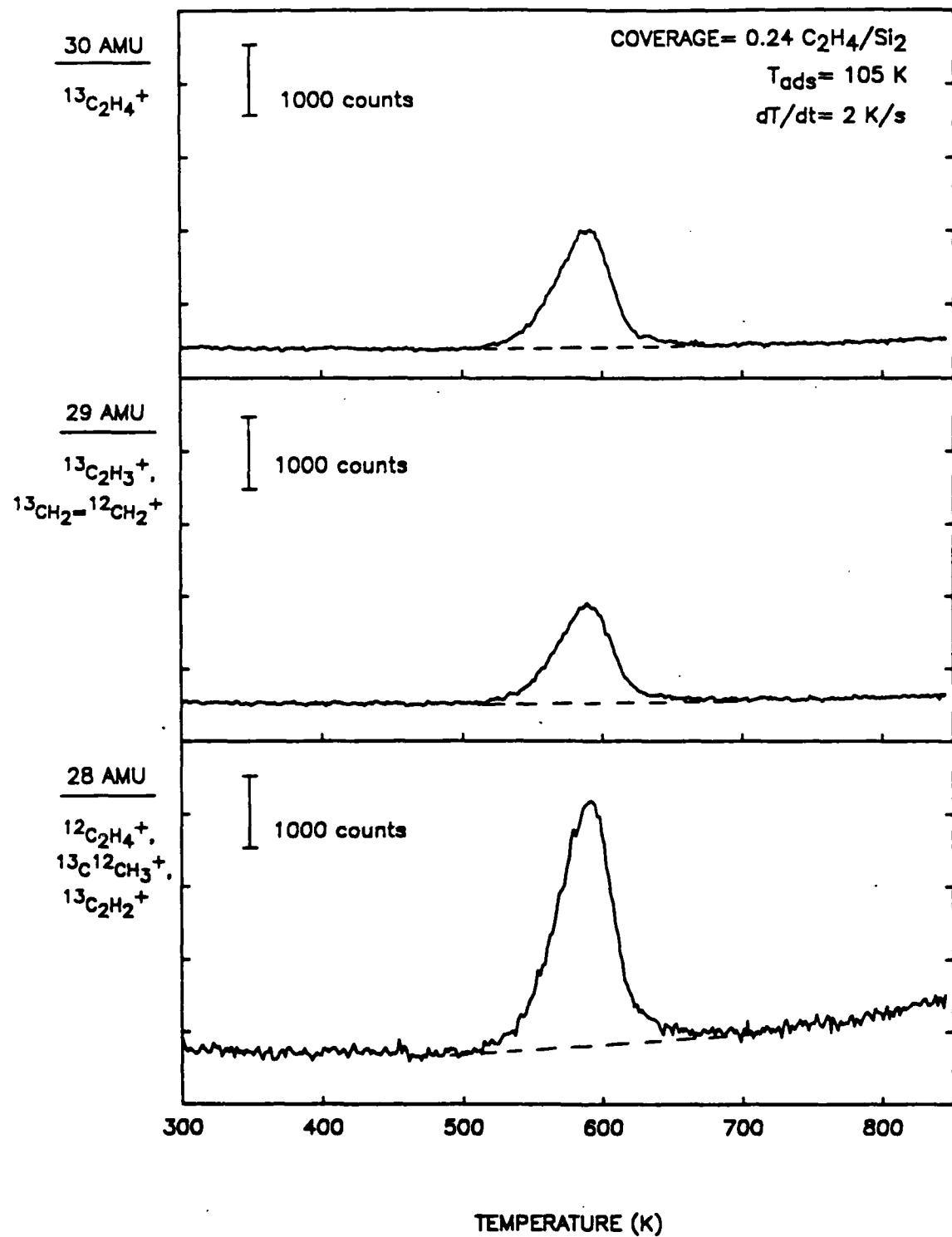
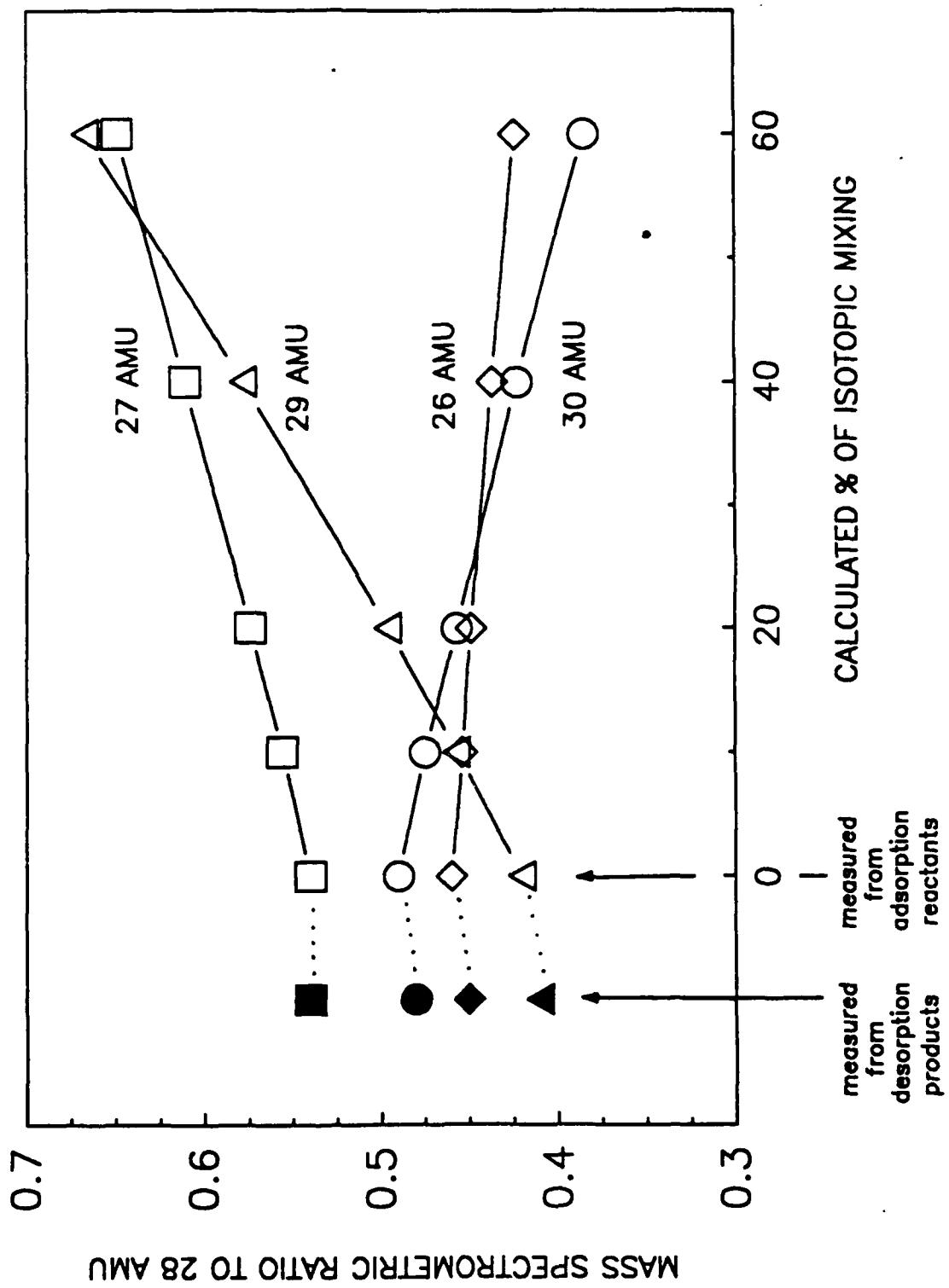
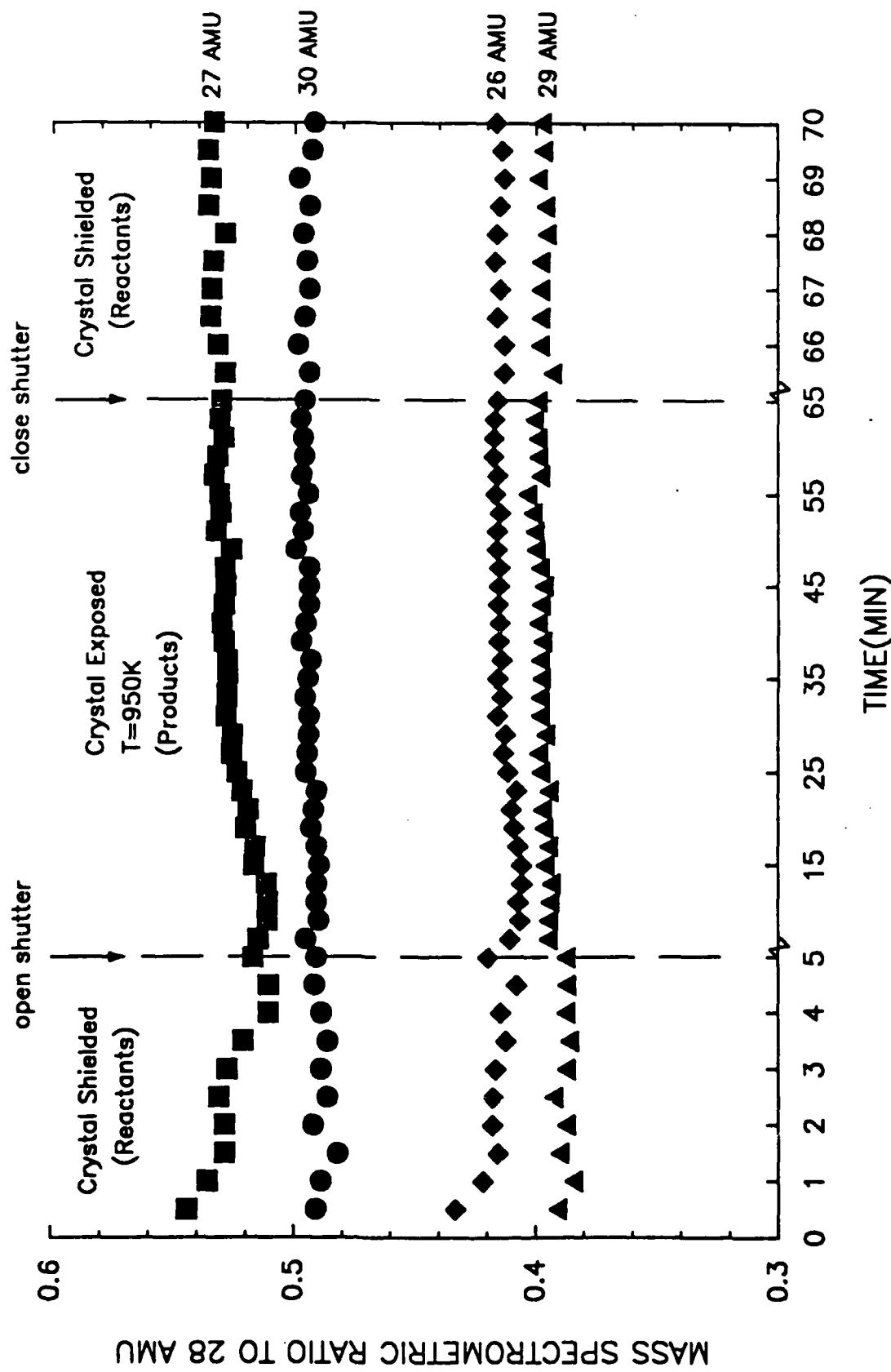


Figure 3
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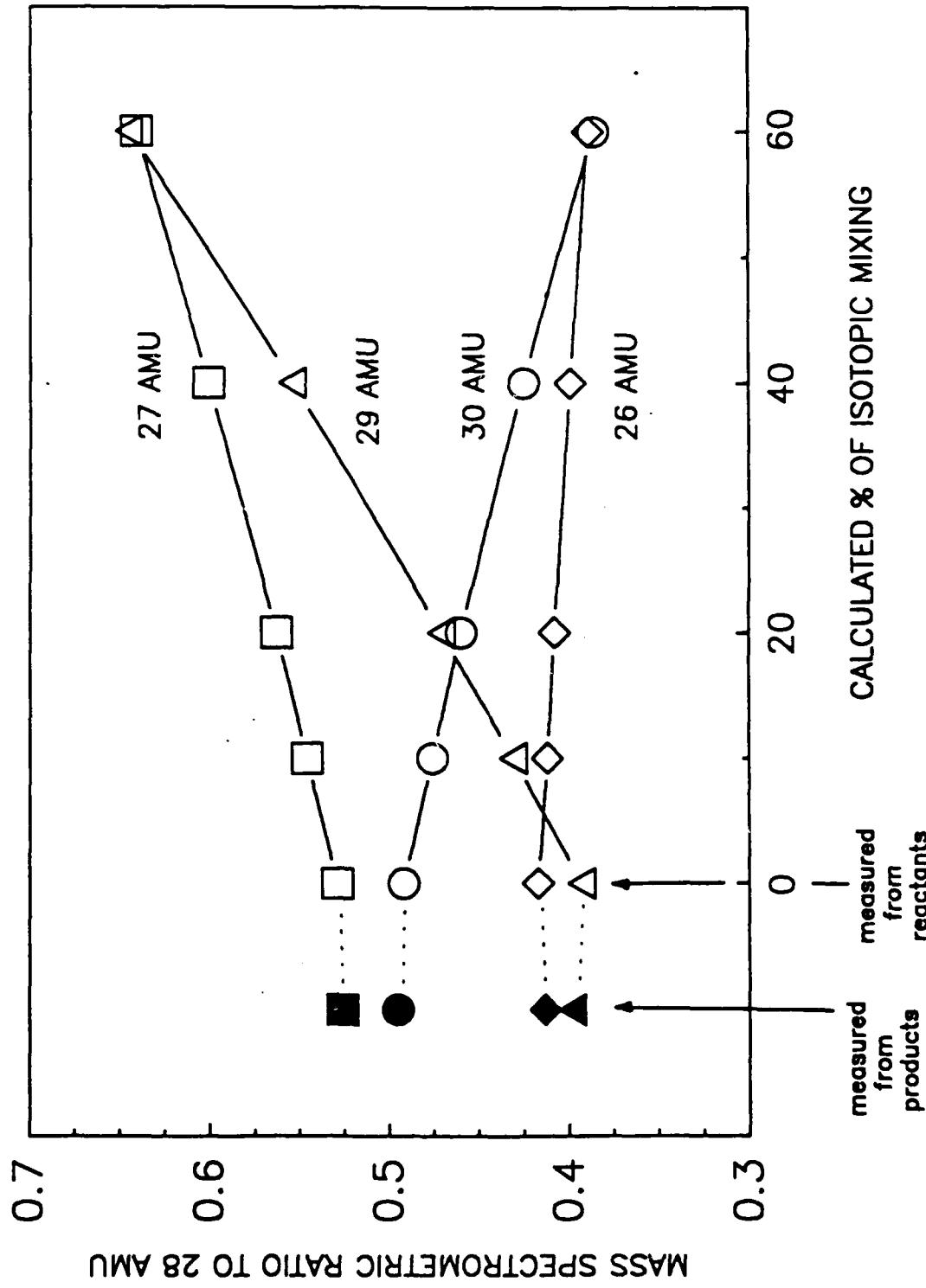
SENSITIVITY OF THE ISOTOPIC MIXING EXPERIMENTS ---
THERMAL DESORPTION OF ETHYLENE



HIGH TEMPERATURE STUDY OF ISOTOPIC MIXING
IN ETHYLENE ON Si(100) AT 950K



SENSITIVITY OF THE ISOTOPIC MIXING EXPERIMENTS ---
DURING ETHYLENE EXPOSURE TO Si(100) AT 950K



AUGER SPECTROSCOPIC STUDY OF CARBON DEPOSITION ON Si(100) FROM C_2H_4 AT 940K

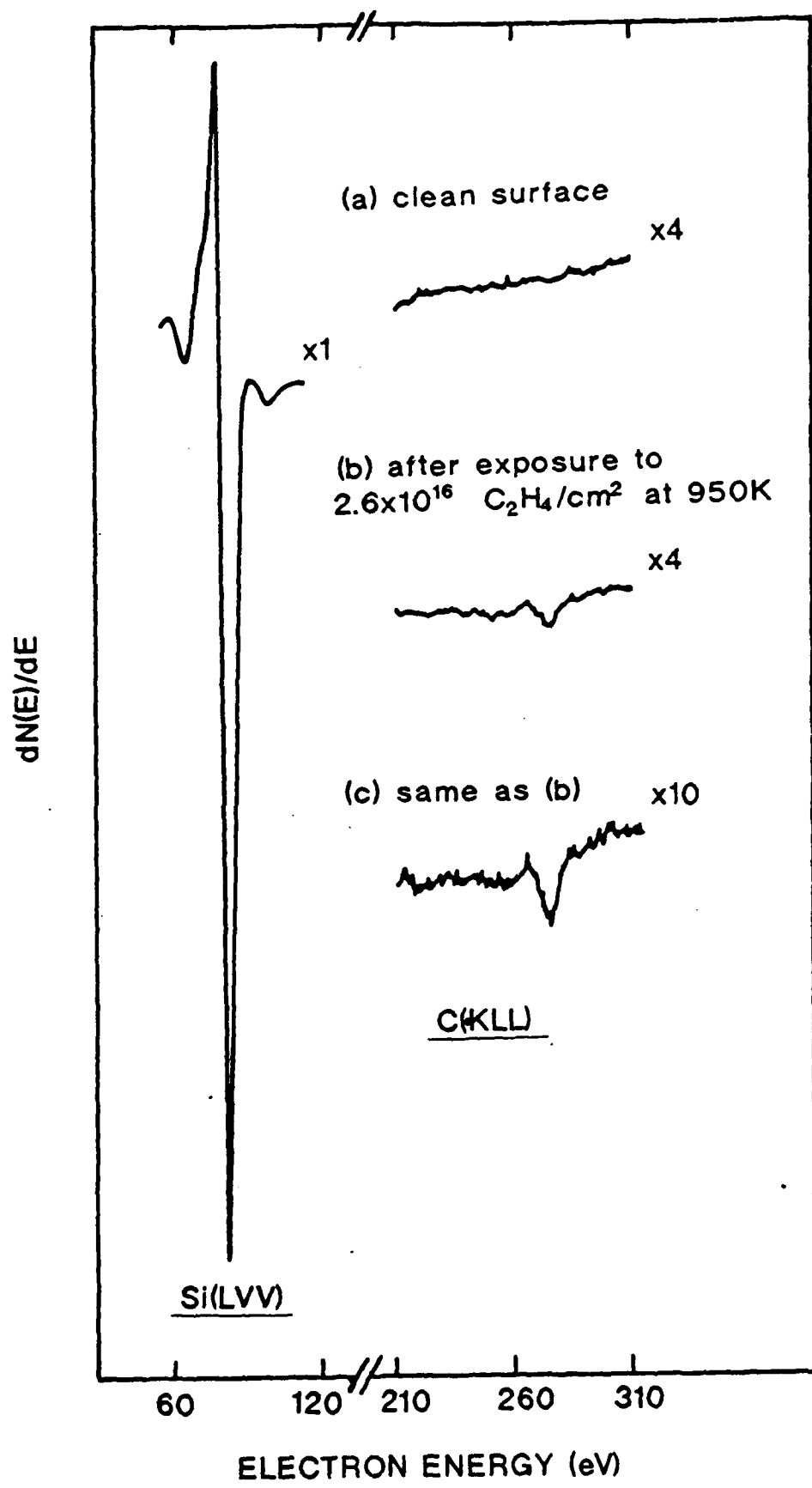


Figure 7
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